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(54) Title: A PROCESS FOR FORMING A TWO-COAT COMPOSITE COATING, THE COMPOSITE COATING AND CHIP RESISTANT COATING COMPOSITION

(57) Abstract: A process for applying two coatings, one on top of the other, to a substrate is provided. A first coating is applied to provide corrosion resistance and a second polyurethane-based coating is applied to the first coating to provide chip resistance. Also, aqueous dispersions of the polyurethane coating compositions are disclosed.

**A PROCESS FOR FORMING A TWO-COAT
COMPOSITE COATING, THE COMPOSITE COATING
AND CHIP RESISTANT COATING COMPOSITION**

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Cross-Reference to Related Applications

This application is a continuation-in-part of U.S. Patent Application Serial No. 09/309,851, filed May 11, 1999, which is hereby incorporated by reference herein.

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Field of the Invention

The present invention is directed to a process for depositing a two-coat composite coating on a substrate where the first coating protects against corrosion and the second coating protects against chipping of the coated composite.

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Background

Multilayered coating composites find use in various industries including the coating and/or painting of various motor vehicles. In these industries, and in the automotive industry in particular, considerable efforts have been expended to develop coating compositions with improved performance and aesthetic properties. In the automotive industry, for example, numerous approaches have been advanced to achieve improved chip resistance and corrosion protection. These efforts have included, for example, applying multilayered coating composites having from 2 up to 6 or more coating layers over the substrate. These coating layers can serve to protect the substrate and/or to provide a decorative finish.

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Multilayered coating composites for metal substrates like those in the automobile industry have involved applying an initial resinous coating layer to the substrate to protect the metal substrate from corrosion. These coatings may be applied by either electrophoretic or non-electrophoretic coating methods.

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Electrodeposition has become increasingly important in the coatings industry because by comparison with non-electrophoretic coating means, electrodeposition offers higher paint utilization, outstanding corrosion protection, low environmental contamination, and a highly automated process. Two-coat application by the electrodeposition process is known in the art. For example in U.S. Patent Nos. 4,988,420; 4,840,715 and 5,275,707 different types of electroconductive pigments are added to a first electrodeposited acrylic resinous coating, and a second electrodeposition coating is applied over the conductive first

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electrodeposited acrylic coating. Typically, these second electrodeposition coatings have been applied for durability and decorative purposes.

Non-electrophoretic coatings, such as sprayable coatings, however, are still widely used throughout the coatings industry because of the relatively low equipment and operating costs associated therewith.

A spray applied chip resistant coating layer protects the surface of the substrates from losing paint through chipping when the substrate of the vehicle is hit with solid debris such as gravel and stones. The art for achieving chip resistance from spray applied primer coatings has postulated that reducing the differential in impact energy between multiple coating layers should improve chip resistance of the coating. This is especially the situation for those coating layers with excessive difference of hardness between them. This reduction in the differential would lessen delamination between the coatings such as between the undercoat and an intermediate coat and a top coat or an undercoat and an intermediate coat.

In U.S. Patent No. 5,674,560, this differential is reduced through a chip resistant polyolefin type of primer that is spray applied over a cationic or anionic electrodeposited coated film before application of a soft intermediate polyester film. The reduction of the differential in impact energy is reportedly maximized when the polyolefin primer is applied over the softer anionic electrodeposited film as opposed to a cationic electrodeposited film.

Therefore, even though the art recognizes that cationic electrodeposited coatings provide better corrosion resistance than anionic electrodeposited coatings, further improvements in chip resistance in a multilayered coating system may be at odds with or involve sacrificing some corrosion resistance by using the anionic electrodeposited coating for corrosion protection. Furthermore, even though the art recognizes that electrophoretic coatings provide many advantages over non-electrophoretic coatings, improvements to each are still sought because of the widespread use of both.

Accordingly, the need exists for a process and system for improved multiple layer coatings with both good chip resistance and corrosion protection that may be applied onto the substrate by either electrophoretic or non-electrophoretic coating methods.

SUMMARY OF THE INVENTION

The present invention provides a process of coating substrates, comprising:

- (a) applying a first coating composition comprising at least one curable resin to at least a portion of a surface of a substrate to form a first coating thereon;
- 5 (b) at least partially curing the first coating;
- (c) applying a second coating composition over at least a portion of the first coating, the second coating composition comprising a curable polyurethane resin that contains a polymeric segment derived from an active hydrogen-containing polymer having a glass transition temperature of 0°C or less and a number average molecular weight of 400-
10 4000 grams per mole; and
- (d) at least partially curing the second coating.

An article coated by the process of the invention is also provided.

Also provided is a substantially solvent free aqueous composition comprising a curable polyurethane resin containing ionic salt groups dispersed in an aqueous medium
15 which is the reaction product of:

- (a) a polyisocyanate and
- (b) an active hydrogen-containing polymer having a glass transition temperature of 0°C or less and a number average molecular weight of 400 to 4000.

Also provided is a multicomponent composite coating, comprising:

- 20 (a) a first coating composition applied on at least a portion of a substrate, the first coating composition comprising a curable resin; and
- (b) a second coating composition applied over at least a portion of the first coating composition, the second coating composition comprising a curable polyurethane resin that contains a polymeric segment derived from an active hydrogen-
25 containing polymer having a glass transition temperature of 0°C or less and a number average molecular weight of 400-4000 grams per mole.

DETAILED DESCRIPTION OF THE INVENTION

The use of numerical values in the various ranges specified in this application,
30 unless expressly indicated otherwise, are stated as approximations as though the minimum and maximum values within the stated ranges were both preceded by the word "about". In this manner slight variations above and below the stated ranges can be used to achieve

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substantially the same results as values within the ranges. Also, the disclosure of these ranges is intended as a continuous range including every value between the minimum and maximum values.

In the process of the present invention described herein, each of the first and second coatings may be deposited on the substrate by any means known to one of ordinary skill in the art, such as, for example, by dip coating, direct roll coating, reverse roll coating, curtain coating, spray coating, brush coating, and electrophoretic deposition. For example, as set forth in the examples provided herein, both the first and second coating may be electrophoretically applied onto the substrate. Alternatively, both the first and second coating may be spray applied onto the substrate. Moreover, the first and second coating may be applied onto the substrate by different coating methods. For example, the first coating may be electrophoretically applied on the substrate while the second coating may be spray applied thereover, which is preferred, and vice versa. Accordingly, although this detailed description places particular emphasis on the ability of the present coating compositions to be electrophoretically applied onto a substrate, these electrophoretic processes are only non-limiting examples illustrating the applicability of the present invention; one of ordinary skill in the art will recognize that the first and second coatings of the present invention need not be electrically conductive, and that other non-electrophoretic coating methods may be employed in the present invention.

The first step in the process of the invention is applying a first coating composition onto at least a portion of the surface of the substrate to form a first coating thereon. The first coating composition comprises at least one curable resin, and may be applied onto the substrate by any coating method known to one of ordinary skill in the art. In one embodiment, the first coating composition is electrodeposited onto the surface of an electrically conductive substrate to form an electrically conductive coating. In this embodiment, the first coating composition comprises at least one curable ionic resin and at least one electrically conductive pigment. Where the first coating composition is ionic, the composition may be an anionic electrodepositable composition or a cationic electrodepositable composition, which is preferred. The anionic and cationic electrodepositable compositions that can be used are those that provide high throwpower and good corrosion resistance. These compositions are well known in the art.

Examples of ionic resins suitable for use in anionic electrodepositable coating compositions are base-solubilized, carboxylic acid containing polymers such as the reaction product or adduct of a drying oil or semi-drying fatty acid ester with a dicarboxylic acid or anhydride; and the reaction product of a fatty acid ester, unsaturated acid or anhydride and any additional unsaturated modifying materials which are further reacted with polyol. Also suitable are the at least partially neutralized interpolymers of hydroxy-alkyl esters of unsaturated carboxylic acids, unsaturated carboxylic acid and at least one other ethylenically unsaturated monomer. Still another suitable electrodepositable resin comprises an alkyd-aminoplast vehicle, i.e., a vehicle containing an alkyd resin and an amine-aldehyde resin.

Yet, another anionic electrodepositable resin composition comprises mixed esters of a resinous polyol. These compositions are described in detail in U.S. Patent No. 3,749,657 at col. 9, lines 1 to 75 and col. 10, lines 1 to 13, all of which are herein incorporated by reference. Other acid functional polymers also can be used such as phosphatized polyepoxide or phosphatized acrylic polymers as are well known to those skilled in the art.

Examples of ionic resins suitable for use in cationic electrodepositable coating compositions include amine salt group-containing resins such as the acid-solubilized reaction products of polyepoxides and primary or secondary amines such as those described in U.S. Patent Nos. 3,663,389; 3,984,299; 3,947,338 and 3,947,339. Usually, these amine salt group-containing resins are used in combination with a blocked isocyanate curing agent. The isocyanate can be fully blocked as described in the aforementioned U.S. Patent No. 3,984,299 or the isocyanate can be partially blocked and reacted with the resin backbone such as described in U.S. Patent No. 3,947,338. Also, one-component compositions as described in U.S. Patent No. 4,134,866 and DE-OS No. 2,707,405 can be used as the film-forming resin. Besides the epoxy-amine reaction products, film-forming resins can also be selected from cationic acrylic resins such as those described in U.S. Patent Nos. 3,455,806 and 3,928,157.

Besides amine salt group-containing resins, quaternary ammonium salt group-containing resins can also be employed. Examples of these resins are those that are formed from reacting an organic polyepoxide with a tertiary amine salt. Such resins are described in U.S. Patent Nos. 3,962,165; 3,975,346 and 4,001,101. Examples of other cationic resins are ternary sulfonium salt group-containing resins and quaternary phosphonium salt-group containing resins such as those described in U.S. Patent Nos. 3,793,278 and 3,984,922, respectively. Also, film-forming resins which cure via transesterification such as described in

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European Application No. 12463 can be used. Further, cationic compositions prepared from Mannich bases such as described in U.S. Patent No. 4,134,932 can be used.

Useful resins include positively charged resins that contain primary and/or secondary amine groups. Such resins are described in U.S. Patent Nos. 3,663,389; 3,947,339 and 4,116,900. In U.S. Patent No. 3,947,339, a polyketimine derivative of a polyamine such as diethylenetriamine or triethylenetetraamine is reacted with a polyepoxide. When the reaction product is neutralized with acid and dispersed in water, free primary amine groups are generated. Also, equivalent products are formed when polyepoxide is reacted with excess polyamines such as diethylenetriamine and triethylenetetraamine and the excess polyamine vacuum stripped from the reaction mixture. Such products are described in U.S. Patent Nos. 3,663,389 and 4,116,900.

Electrodepositable compositions such as disclosed in U.S. Patent No. 5,767,191 containing oleic acid and abietic acid and U.S. Patent No. 4,891,111 containing alkylated polyether are preferred.

The curable resin of the first coating composition generally is present in the composition in amounts of about 1 to about 60 percent by weight, preferably about 5 to about 25 based on total weight of the first coating composition.

The first coating composition is preferably in the form of an aqueous dispersion. The term "dispersion" is a two-phase transparent, translucent or opaque resinous system in which the resin is in the dispersed phase and the water is in the continuous phase. The average particle size of the resinous phase is generally less than 1.0 microns and usually less than 0.5 microns, preferably less than 0.15 microns.

The concentration of the resinous phase in the aqueous medium is at least 1 and usually from about 2 to about 60 percent by weight based on total weight of the aqueous dispersion.

Where the first coating composition is an ionic electrodepositable composition, the composition may further comprise at least one electroconductive pigment to make the resultant coating electroconductive. Suitable electroconductive pigments include electrically conductive carbon black pigments. Generally, the carbon blacks can be any one or a blend of carbon blacks ranging from those that are known as higher conductive carbon blacks, i.e. those with a BET surface area greater than 500 m²/gram and DBP adsorption number (determined in accordance with ASTM D2414-93) of 200 to 600 ml/100 g to those with

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lower DBP numbers on the order of 30 to 120 ml/100 gram such as those with DBP numbers of 40 to 80 ml/100 grams.

Examples of commercially available carbon blacks include Cabot Monarch™ 1300, Cabot XC-72R, Black Pearls 2000 and Vulcan XC 72 sold by Cabot Corporation; Acheson
5 Electrodag™ 230 sold by Acheson Colloids Co.; Columbian Raven™ 3500 sold by Columbian Carbon Co.; and Printex™ XE 2, Printex 200, Printex L and Printex L6 sold by DeGussa Corporation, Pigments Group. Suitable carbon blacks are also described in U.S. Patent No. 5,733,962, which is incorporated by reference herein.

Also, electrically conductive silica pigments may be used. Examples include
10 "Aerosil 200" sold by Japan Aerosil Co., Ltd., and "Syloid 161", "Syloid 244", "Syloid 308", "Syloid 404" and "Syloid 978" made by Fuji Davison Co., Ltd.

Mixtures of different electroconductive pigments can be used.

Where the composition containing the first coating is intended to be electroconductive, the amount of electroconductive pigment in the electrodepositable
15 composition can vary depending on specific type of pigment that is used, but the level needs to be effective to provide an electrodeposited coating with a conductivity of greater than or equal to 10^{-12} mhos/cm. Stated another way the electrodeposited coating should have a resistivity of less than or equal to 10^{12} ohms-cm., preferably a resistance of less than or equal to 10^8 ohms at typical film builds or thicknesses for electrodeposited coatings. This
20 level is necessary so that upon curing or partial curing the coating becomes electroconductive. Preferably, curing is by heating at a temperature of at least 120°C (248°F). Typically, the electroconductive pigment content in the electrodepositable composition is from 5 to 25 percent by weight based on total solids of the electrodeposition composition.

25 Most electroconductive substrates, especially metal substrates such as steel, zinc, aluminum, copper, magnesium, or the like and galvanized metals such as any galvanized steels and the like whether hot dip galvanized or electrogalvanized or other galvanizing method can be coated with the first coating composition. Steel substrates are preferred. It is customary to pretreat the substrate with a phosphate conversion coating, usually a zinc
30 phosphate conversion coating, followed by a rinse that seals the conversion coating. Pretreatments are well known to those skilled in the art. Examples of suitable pretreatment

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compositions are disclosed in U.S. Patent Nos. 4,793,867 and 5,588,989, which is incorporated by reference herein.

As discussed above and as further set forth in the examples below, the compositions containing the first coating may be applied to the substrate by any coating process known to one of ordinary skill in the art. When the composition containing the first coating is intended to be applied electrophoretically, for example, the aqueous dispersion of the electrodepositable composition is placed in contact with an electrically conductive anode and cathode. Upon passage of an electric current between the anode and cathode, an adherent film of the electrodepositable composition will deposit in a substantially continuous manner on either the anode or the cathode depending on whether the composition is anionically or cationically electrodepositable. Electrodeposition is usually carried out at a constant voltage in the range of from about 1 volt to several thousand volts, typically between 50 and 500 volts. Current density is usually between about 1.0 ampere and 15 amperes per square foot (10.8 to 161.5 amperes per square meter).

After the first coating composition is applied to the substrate, the coating is at least partially cured, typically by heating. Temperatures usually range from 200°F to 400°F (93.3°C to 204.4°C), preferably from 300°F to 375°F (149° to 191°C) for a period of time ranging from 10 to 60 minutes. The thickness of the resultant cured coating or film is usually from about 10 to 50 microns.

The heating or baking of the coating can also be performed by means of infrared radiation ("IR"). Generally, there are three categories of IR. These categories are: near-IR (short wavelength) having a peak wavelength from 0.75 to 2.5 microns ("u") (750 to 2500 nanometers); intermediate-IR (medium wavelength) having a peak wavelength from 2.5 to 4 u (2500 to 4000 nanometers), and far-IR (long wavelength) having a peak wavelength from 4 to 1000 u (4000 to 100,000 nanometers). Any combination or all of these categories of IR can be used for the heating to at least partially cure the coating.

Curing can be done in a selective manner. For example, at least one predetermined area of the first coating composition can be selectively heated by IR, for example, the exterior surfaces of an automobile body, where such predetermined area is to be coated with the second coating composition. The interior surfaces of the coated substrate are not exposed to the IR and as a result, the first coating is not cured on the interior surfaces and does not become electroconductive. Hence, the deposition of the second electrodeposited

coating layer is only on the exterior surfaces that are electrically conductive. With this treatment, substrates like an automobile body have the cured, conductive, first electrodeposited coating on exterior surfaces and the uncured, nonconductive, first electrodeposited coating on interior surfaces. Upon application of the second

5 electrodeposited coating and curing of both electrodeposited coatings, the exterior surface of the automobile body will have both the first and second electrodeposited coatings and good corrosion and chip resistance where it is needed most. The interior surface will only have the first electrodeposited coating and corrosion resistance but little chip resistance. Since the interior surfaces will not be exposed to road debris, chip resistance is not needed.

10 When IR heating is used with complex shapes such as automobile bodies, it is preferable to dry the substrate coated with the first coating composition for 2 to 20 minutes, in a standard oven such as a convection, electric, or gas fired oven before exposing the substrate to IR. When the first coating contains electroconductive pigment, the drying step can be at a temperature sufficient to remove water but not sufficient to cure the coating such

15 that it becomes conductive. Generally, the temperature is less than 120°C.

IR heating can be conducted from 10 seconds to 2 hours, usually from 5 to 20 minutes. Temperatures can range from greater than 120°C to 220°C (248°F to 428°F) and preferably from 130°C to 190°C (266°F to 374°F).

After application of the first coating, a second coating is applied over at least a

20 portion of the first coating, and, preferably, applied such that the second coating completely covers the first coating. The second coating composition is typically a low organic solvent content coating. Preferably, the second coating composition is substantially solvent free and spray applied, for example by electrostatic application, over at least a portion of the first coating. The second coating is deposited from a composition comprising a curable

25 polyurethane resin that contains a polymeric segment derived from an active hydrogen-containing polymer having a glass transition temperature of 0°C or less and a number average molecular weight of 400-4000 grams per mole. The second coating may, but need not, be ionic. When the first coating provides corrosion resistance, the second coating provides chip resistance. When the polyurethane resin is ionic, the resin can be anionic or

30 cationic, but preferably is cationic and the composition is cationically electrodepositable. The polyurethane will have a molecular weight (M_w) of less than 100,000, preferably less than 50,000 and most preferably from 10,000 to 40,000. The polyurethane also has active

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hydrogen functionality, i.e., hydroxyl, primary or secondary amine, and typically has an active hydrogen equivalent weight of 800 to 2500 grams per equivalent.

As used herein, the term "low organic solvent content" is meant to include those compositions having a solvent content of less than 20 percent by weight and typically less than 10 percent by weight. The term "substantially solvent free" is meant to include those compositions having a solvent content of less than 7 percent by weight, typically less than 2 percent by weight, and may be less than 1 percent by weight. In one embodiment, the second coating is free from solvent.

By the term "polyurethane", as used herein, the meaning is intended to include polyurethanes as well as polyureas, and poly(urethane-ureas).

The molecular weight of the polyurethane and other polymeric materials used in the practice of the invention is determined by gel permeation chromatography using a polystyrene standard.

Preferably, the polyurethane resin is prepared from the reaction product of components comprising one or more polyisocyanates and one or more active hydrogen-containing polymers in a manner well known to those skilled in the art.

Suitable polyisocyanates used for preparing the polyurethanes include those that have aliphatically, cycloaliphatically, araliphatically, and/or aromatically bound isocyanate groups. Preferably, the polyisocyanate is aliphatic or cycloaliphatic.

Examples of suitable aliphatic and cycloaliphatic polyisocyanates include 4,4-methylenebisdicyclohexyl diisocyanate (hydrogenated MDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), methylenebis(cyclohexyl isocyanate) and cyclohexylene diisocyanate (hydrogenated XDI).

Examples of suitable aromatic polyisocyanates include tolylene diisocyanate (TDI) (i.e., 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate or a mixture thereof), diphenylmethane-4,4-diisocyanate (MDI), naphthalene-1,5-diisocyanate (NDI), 3,3-dimethyl-4,4-biphenylene diisocyanate (TODI), crude TDI (i.e., a mixture of TDI and an oligomer thereof), polymethylenepolyphenyl polyisocyanate, crude MDI (i.e., a mixture of MDI and an oligomer thereof), xylylene diisocyanate (XDI) and phenylene diisocyanate.

Polyisocyanate derivatives prepared from hexamethylene diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane ("IPDI"), including isocyanurates thereof, and/or 4,4'-bis(isocyanatocyclohexyl)methane also are suitable.

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The amount of polyisocyanate used to make the polyurethanes is typically from 10 to 60 percent by weight, and preferably from 20 to 50 percent by weight based on total weight of the reactants used to make the polyurethane.

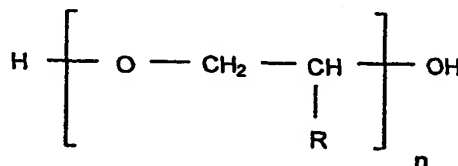
When the polyurethane is ionic, the active hydrogen-containing material for reaction with the polyisocyanate to form the cationic or anionic polyurethane comprises one or more active hydrogen-containing polymers. These materials preferably have an average active hydrogen functionality ranging from about 2 to 8, preferably from about 2 to 4, and a number average molecular weight ranging preferably from about 400 to 10,000, more preferably from 400 to 4,000, and a glass transition temperature (T_g) of 0°C or less.

10 Polyether polyols are preferred.

The term "active hydrogen" means those groups that are reactive with isocyanates as determined by the Zerewitnoff test as is described in the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, Vol. 49, page 3181 (1927). Preferably, the active hydrogens are hydroxyl, primary amine and secondary amine. The T_g for many polyethers are available in the literature. Also helpful in determining the T_g is the Clash-Berg method, described in Advances in Polyurethane Technology, Burst et al., Wiley & Sons, 1968, pages 88ff.

Examples of polyether polyols are polyalkylene ether polyols which include those having the following structural formula:

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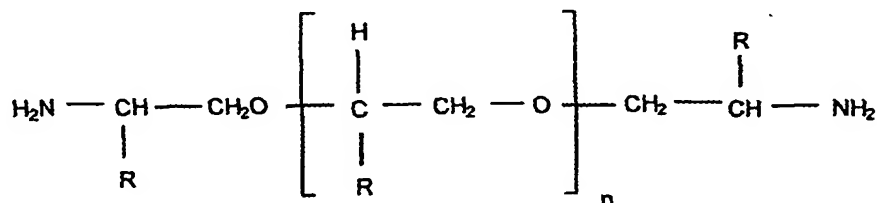


where the substituent R is hydrogen or lower alkyl containing from 1 to 5 carbon atoms including mixed substituents, and n is typically from 5 to 200. Included are poly(oxytetramethylene) glycols, poly(oxyethylene) glycols, poly(oxy-1,2-propylene) glycols and the reaction products of ethylene glycol with a mixture of 1,2-propylene oxide and ethylene oxide. These materials are obtained by the polymerization of alkylene oxides such as ethylene oxide, propylene oxide and tetrahydrofuran.

Also, polyethers obtained from the oxyalkylation of various polyols, for example, diols such as 1,6-hexanediol or higher polyols such as trimethylolpropane and sorbitol can

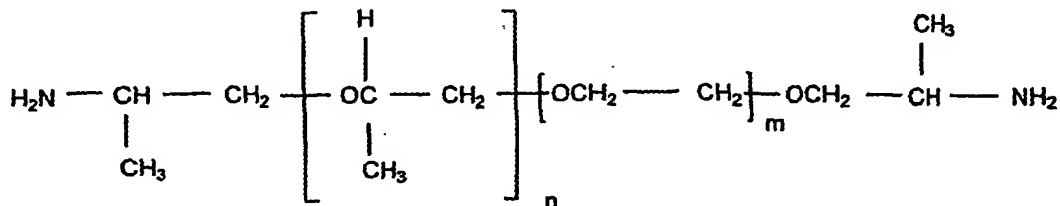
be used. One commonly utilized oxyalkylation method is by reacting a polyol with alkylene oxide such as ethylene or propylene oxide in the presence of an acidic or basic catalyst.

Examples of other active hydrogen-containing polyethers are polyoxyalkylenepolyamines. The preferred polyoxyalkylenepolyamines are those of the structure:



wherein R can be the same or different and is selected from the group consisting of hydrogen, lower alkyl radicals having from 1 to 6 carbon atoms, and n represents an integer of from about 1 to 50, preferably 1 to 35. A number of such polyoxyalkylenepolyamines are described in more detail in U.S. Patent No. 3,236,895, column 2, lines 40-72; methods of preparation of the polyoxyalkylenepolyamines are illustrated in the patent in Examples 4, 5, 6 and 8-12 in columns 4 to 9 thereof; the aforementioned portions of U.S. Patent No. 3,236,895 hereby being incorporated by reference.

Mixed polyoxyalkylenepolyamines can be used, that is, those in which the oxyalkylene group can be selected from more than one moiety. Examples would be mixed polyoxyethylene-propylenepolyamines such as those having the following structural formula:

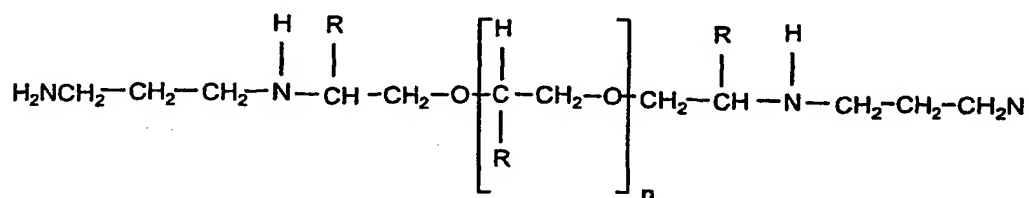


wherein n+m is equal to 1 to 50, preferably 1 to 35, m is equal to 1 to 49, preferably 1 to 34, and n is equal to 1 to 34.

Besides the polyoxyalkylenepolyamines mentioned above, derivatives of polyoxyalkylenepolyamines may also be usable. Examples of suitable derivatives would be aminoalkylene derivatives that are prepared by reacting polyoxyalkylenepolyamines such as

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those mentioned above with acrylonitrile followed by hydrogenation of the reaction product. An example of a suitable derivative would be that of the following structural formula:



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wherein R can be the same or different and is selected from the group consisting of hydrogen, lower alkyl radicals having from 1 to 6 carbon atoms, and n represents an integer of from about 1 to 50, preferably 1 to 35.

Therefore, in the practice of the invention, where the expression
 10 "polyoxyalkylenepolyamines" is used, what is intended are polyamines containing both oxyalkylene groups and at least two amine groups, preferably primary amine groups, per molecule. Primary amines are considered to be monofunctional.

The preferred active hydrogen-containing polyethers are polyoxytetramethylene diols, also known as polytetrahydrofuran, and polyoxypropylenediamine or mixed
 15 polyoxyethylene-propylenediamines.

For mixed oxyethylene-propylene groups in the polyether segment, it is preferred that the oxypropylene content be at least 60 weight percent, more preferably at least 70 weight percent, and most preferably at least 80 weight percent of the polyether segment.

The polyether segment can be derived from a single polyether polyol or polyamine
 20 or various blends thereof. Preferred are blends of polyether polyols such as polyoxytetramethylene diol and polyether polyamines such as polyoxypropylenediamine in weight ratios of 0.5-10:1, preferably 1 to 7:1.

Besides active hydrogen-containing polyethers, other active hydrogen-containing materials can be reacted with the polyisocyanate to provide the soft segment. Examples
 25 include polycarbonate diols, polyester diols, hydroxyl-containing polydiene polymers, hydroxyl-containing acrylic polymers, and mixtures thereof.

Examples of polyester polyols and hydroxyl containing acrylic polymers are described in U.S. Patent Nos. 3,962,522 and 4,034,017, respectively. Examples of polycarbonate polyols are described in U.S. Patent No. 4,692,383 in col. 1, line 58 to col.

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4, line 14. Examples of hydroxyl-containing polydiene polymers are disclosed in U.S. Patent No. 5,863,646, col. 2, lines 11-54. These polymeric polyols will have number average molecular weights of from 400 to 10,000.

The amount of the active hydrogen-containing polymer that is used to prepare the polyurethane is at least 30, preferably at least 35, and more preferably from 35 to 50 percent by weight based on total weight of the reactants used to make the polyurethane. Low molecular weight polyols such as those having two to four hydroxyl groups and molecular weights of less than 400, preferably less than 250 and usually between 62 and 250 can also be included as reactants for preparing the polyurethane. Specific examples include alkylene diols having 1 to 10 carbon atoms such as ethylene glycol, 1,2-propylene glycol, 1,4-butanediol, trimethylolpropane, glycerol, pentaerythritol and sorbitol. Examples of other low molecular weight polyols are ether polyols such as diethylene glycol and ethoxylated bisphenol A.

The low molecular weight polyols are used in amounts up to 30 percent by weight, preferably from 0.5 to 10 percent by weight based on weight of the reactants used to make the polyurethane.

The prepolymer may also have ionizable groups that can be ionized for solubilizing the polymer in water. For the purposes of this invention, the term "ionizable" means a group capable of becoming ionic, i.e., capable of dissociating into ions or becoming electrically charged.

For the cationic polyurethanes, the ionizable moiety is typically a tertiary amine group that can be incorporated into the polyurethane by reaction with an active hydrogen-containing compound. The amine is neutralized with acid to form the amine salt groups. Such compounds include aminoalcohols such as dimethylaminoethanol, dimethylaminopropanol, aminopropyldiethanolamine, diethylaminopropylamine, hydroxyalkylmorpholine like hydroxyethylmorpholine, and hydroxyalkylpiperazine like hydroxyethylpiperazine, and the like and mixtures thereof. The amount of amine introduced into the polymer typically is that sufficient to give 0.1 to 1, preferably 0.2 to 0.5 milliequivalents (meqs) of amine per gram of resin solids as determined by titration.

For the anionic polyurethane, the ionizable moiety is an acid group which typically is incorporated into the polyurethane by reaction with an active hydrogen-containing compound. The acid is neutralized with base to form the carboxylate salt group. Examples

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of anionic groups are $-\text{OSO}_3^-$, $-\text{COO}^-$, $-\text{OPO}_3^{2-}$, $-\text{SO}_2\text{O}^-$, $-\text{POO}^-$; and PO_3^{2-} , with COO^- being preferred.

Suitable materials for introducing acid groups into the anionic polyurethane are hydroxy and mercapto carboxylic acids. Specific examples include dimethylolpropionic acid, which is preferred, glycolic acid and lactic acid. Other examples of compounds which contain active hydrogens and acid groups are amino carboxylic acids, amino hydroxy carboxylic acids, sulfonic acids, hydroxy sulfonic acids and amino sulfonic acids. Examples include oxaluric acid, anilido acetic acid, glycine, 6-amino-caprylic acid, reaction product of ethanolamine and acrylic acid, hydroxyethylpropionic acid, 2-hydroxy-ethane sulfonic acid and sulphanilic acid. Amino acids must be used in the presence of base such as potassium hydroxide or a tertiary amine. The amount of acid incorporated into the polymer typically is that sufficient to give the polymer 0.1 to 1, preferably 0.2 to 0.5 meqs of acid per gram of resin solids as determined by titration.

The amine or the acid groups are neutralized with acid and base, respectively. Neutralization can range from 0.1 to 1.0, preferably 0.4 to 0.8, of the total theoretical neutralization equivalent.

For the cationic polyurethanes, suitable neutralizing agents are organic acids such as acetic acid, hydroxyacetic acid, propionic acid, lactic acid, formic acid, tartaric acid, sulfamic acid and dimethylolpropionic acid that is preferred, as well as inorganic acids such as sulfuric acid, hydrochloric acid and phosphoric acid.

For anionic polyurethanes, suitable neutralizing agents include inorganic and organic bases such as sodium hydroxide, potassium hydroxide, ammonia and amines. Suitable amines include alkanolamines such as monoethanolamine, diethanolamine, dimethylaminoethanol, triethanolamine, diisopropanolamine, triisopropanolamine, and the like; alkylamines such as diethylamine, triethylamine, diisopropylamine, tributylamine and the like; trimethylamine, diethylmethylamine, methyldiethanol-amine, triethanolamine, and the like. The appropriate amount of the neutralizing agent is about 0.1 to 1.0 times, preferably 0.4 to 0.8 times the total theoretical neutralization equivalent.

To achieve optimum chip resistance and durability, the polyurethane is curable or thermosetting. As such, it is used with a curing or crosslinking agent such as a capped or blocked isocyanate, which is preferred for cationic compositions, or an aminoplast, which is preferred for anionic compositions.

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The polyisocyanate may be fully capped with essentially no free isocyanate groups and present as a separate component or it may be partially capped and reacted with hydroxyl or amine groups in the polyurethane backbone. Examples of suitable polyisocyanates and capping agents are those described in U.S. Patent No. 3,947,339, which is incorporated by reference herein.

When the crosslinking agent contains free isocyanate groups, the film-forming composition is preferably a two-package composition (one package comprising the crosslinking agent and the other comprising the hydroxyl functional polymer) in order to maintain storage stability. Fully capped polyisocyanates are described in U.S. Patent No. 3,984,299, which is incorporated by reference herein.

The polyisocyanate can be an aliphatic, cycloaliphatic or an aromatic polyisocyanate or a mixture of the two. Diisocyanates are preferred, although higher polyisocyanates can be used in place of or in combination with diisocyanates. Aliphatic or cycloaliphatic polyisocyanates are preferred.

Examples of suitable aliphatic diisocyanates are straight chain aliphatic diisocyanates such as 1,4-tetramethylene diisocyanate and 1,6-hexamethylene diisocyanate. Also, cycloaliphatic diisocyanates can be employed. Examples include isophorone diisocyanate and 4,4'-methylene-bis-(cyclohexyl isocyanate). Examples of suitable aromatic diisocyanates are p-phenylene diisocyanate, diphenylmethane-4,4'-diisocyanate and 2,4- or 2,6-toluene diisocyanate. Examples of suitable higher polyisocyanates are triphenylmethane-4,4',4"-triisocyanate, 1,2,4-benzene triisocyanate and polymethylene polyphenyl isocyanate. Biurets and isocyanurates of diisocyanates, including mixtures thereof, such as the isocyanurate of hexamethylene diisocyanate, the biuret of hexamethylene diisocyanate, and the isocyanurate of isophorone diisocyanate are also suitable.

Isocyanate prepolymers, for example, reaction products of polyisocyanates with polyols such as neopentyl glycol and trimethylol propane or with polymeric polyols such as polycaprolactone diols and triols (NCO/OH equivalent ratio greater than one) can also be used.

Any suitable aliphatic, cycloaliphatic, or aromatic alkyl monoalcohol or phenolic compound may be used as a capping agent for the capped polyisocyanate crosslinking agent in the composition of the present invention including, for example, lower aliphatic alcohols

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such as methanol, ethanol, and n-butanol; cycloaliphatic alcohols such as cyclohexanol; aromatic-alkyl alcohols such as phenyl carbinol and methylphenyl carbinol; and phenolic compounds such as phenol itself and substituted phenols wherein the substituents do not affect coating operations, such as cresol and nitrophenol. Glycol ethers may also be used as capping agents. Suitable glycol ethers include ethylene glycol butyl ether, diethylene glycol butyl ether, ethylene glycol methyl ether and propylene glycol methyl ether.

Other suitable capping agents include oximes such as methyl ethyl ketoxime, acetone oxime and cyclohexanone oxime, lactams such as epsilon-caprolactam, and amines such as dibutyl amine.

The crosslinking agent is typically present in the thermosetting compositions of the present invention in an amount of at least 10 percent by weight, preferably at least 15 percent by weight, based on total resin solids weight of the coating composition. The crosslinking agent is also typically present in the composition in an amount of less than 60 percent by weight, preferably less than 50 percent by weight, and more preferably less than 40 percent by weight, based on total resin solids weight of the composition. The amount of crosslinking agent present in the thermosetting composition of the present invention may range between any combination of these values, inclusive of the recited values.

The equivalent ratio of hydroxyl groups in the polymer to reactive functional groups in the crosslinking agent is typically within the range of 1:0.5 to 1.5, preferably 1.0 to 1.5.

Aminoplasts are obtained from the reaction of formaldehyde with an amine or amide. The most common amines or amides are melamine, urea, or benzoguanamine, and are preferred. However, condensates with other amines or amides can be used; for example, aldehyde condensates of glycoluril, which give a high melting crystalline product that is useful in powder coatings. While the aldehyde used is most often formaldehyde, other aldehydes such as acetaldehyde, crotonaldehyde, and benzaldehyde may be used.

The aminoplast contains methylol groups and preferably at least a portion of these groups are etherified with an alcohol to modify the cure response. Any monohydric alcohol may be employed for this purpose including methanol, ethanol, butanol, isobutanol, and hexanol.

Preferably, the aminoplasts that are used are melamine-, urea-, glycoluril or benzoguanamine-formaldehyde condensates etherified with an alcohol containing from one to four carbon atoms.

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The aminoplast is present in the composition in amounts of 5 to 60, preferably 15 to 50 percent by weight based on weight of resin solids.

Usually the thermosetting composition will also preferably contain catalysts to accelerate the cure of the crosslinking agent with reactive groups on the polymer(s).

5 Suitable catalysts for aminoplast cure include acids such as acid phosphates and sulfonic acid or a substituted sulfonic acid. Examples include dodecylbenzene sulfonic acid, paratoluene sulfonic acid, and the like. Suitable catalysts for isocyanate cure include organotin compounds such as dibutyltin oxide, dioctyltin oxide, dibutyltin dilaurate, and the like. The catalyst is usually present in an amount of about 0.05 to about 5.0 percent by weight, preferably about 0.08 to about 2.0 percent by weight, based on the total weight of resin solids in the thermosetting composition.

Optional ingredients such as pigments can be present in the polyurethane compositions. Particularly suitable pigments include hiding pigments such as titanium dioxide, zinc oxide, antimony oxide, etc. and organic or inorganic UV opacifying pigments 15 such as iron oxide, transparent red or yellow iron oxide, carbon black, phthalocyanine blue, and the like. Pigments can be present in amounts of up to 35 parts by weight or less based on 100 parts by weight of total solids of the coating composition.

Other optional ingredients are anti-oxidants, UV- absorbers and hindered amine light stabilizers, such as for example, hindered phenols, benzophenones, benzotriazoles, 20 triazoles, triazines, benzoates, piperidinyll compounds and mixtures thereof. These ingredients are typically added in amounts up to about 2% based on the total weight of resin solids of the coating composition. Other optional ingredients include co-solvents, coalescing aids, defoamers, plasticizers, bactericides and the like.

When the polyurethane dispersions of the second coating composition are intended 25 to be electrodeposited over at least a portion of the first coating, the aqueous cationic or anionic polyurethane dispersions are typically electrodeposited on the first coating from an electrodeposition bath having a solids content of 5 to 50 percent by weight. The bath temperature is usually about 15°C to 35°C. The voltage is from 100 to 400 V (load voltage) using the substrate with the first coating as a cathode in the case of the cationic 30 polyurethane or as an anode in the case of the anionic polyurethane. The film thickness of the electrodeposited coating is not particularly restricted and can vary largely depending upon the application of finished product, etc. However, the thickness is usually between 3

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to 70 microns, particularly 15 to 35 microns in terms of cured film thickness. The baking and curing temperature of the coating film is usually from 100°C to 250°C and preferably 140°C to 200°C. As mentioned above in the case of the selective application of the second coating through use of the IR bake of the first coating when the coatings are applied via electrodeposition, the heating or baking after application of the second electrocoat can cure both the first and second electrocoat on surfaces not exposed to IR heating or baking. Also, the baking can complete the cure of the first electrocoat that was exposed to IR and overcoated with the second electrocoat.

10

EXAMPLES

A cationic electrodeposable composition for corrosion protection which results in a conductive coating for a substrate was prepared from the below-described materials in Example 1. These included the blocked polyisocyanate crosslinker prepared according to Example 1A, and the cationic electrodeposable primer resin that along with the blocked polyisocyanate makes up the main vehicle of the composition prepared in Example 1B. The cationic electrodeposable composition was prepared according to Example 1C.

Example 1 Part A: Isocyanate Crosslinker

A blocked polyisocyanate crosslinker was prepared from the following materials:

Material	Parts by weight
Polyisocyanate ¹	1320.00
Methyl isobutyl ketone	369.18
Trimethylol propane	89.46
Dibutyltin dilaurate	1.0
2-(2-Butoxyethoxy)ethanol	1297.84

¹ Polymeric MDI available from DOW CHEMICAL Company, Michigan under the trade designation of PAPI 2940.

The polyisocyanate and methyl isobutyl ketone were charged to a reaction flask under a nitrogen atmosphere and heated to 80°C. Trimethylol propane then was added and the mixture heated to 105°C and held for 30 minutes. The mixture was cooled to 65°C and dibutyltin dilaurate and 2-(2-butoxyethoxy)ethanol were added slowly allowing the reaction

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to exotherm to a temperature between 80 to 110°C and held there until Infrared analysis indicated no unreacted NCO remained.

Example 1 Part B: Cationic Primer Electrodeposition Vehicle

- 5 A cationic aqueous main vehicle was prepared from the following materials. All parts and percentages are by weight unless otherwise indicated.

Material	Parts by weight
EPON 828 ²	1864.07
Bisphenol A-ethylene oxide adduct (1/6 molar ratio) ³	750.00
Bisphenol A	776.23
Methyl isobutyl ketone	109.09
Ethyltriphenyl phosphonium iodide	1.8
Crosslinker from Ex. 1A	2859.26
Diketimine ⁴	110.66
N-methyl ethanolamine	199.48

² Polyglycidyl ether of Bisphenol A, available from Shell Oil and Chemical Co., Houston Texas.

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³ Prepared with materials in accordance with U.S. Patent No. 4,468,307 (Wisner et. al.)

⁴ Diketimine derived from diethylenetriamine and methyl isobutyl ketone (73 % solids in methyl isobutyl ketone).

- 15 The EPON 828, bisphenol A-ethylene oxide adduct, bisphenol A and methyl isobutyl ketone were charged to a reaction vessel and heated under a nitrogen atmosphere to 125°C. Ethyl triphenyl phosphonium iodide was added and the reaction mixture was allowed to exotherm to about 145°C. The reaction was held at a temperature of 145°C for two hours and an epoxy equivalent was obtained. Epoxy equivalent usually stalls close to the target epoxy
- 20 equivalent weight. At this point, the crosslinker, the diketimine and N-methylethanolamine were added in succession. The mixture was allowed to exotherm and then a temperature of 130°C was established and the mixture was held for one hour at 130°C. The resin mixture (6000 parts) was dispersed in aqueous medium by adding it to a mixture of 154.62 parts of sulfamic acid and 3339.88 parts of deionized water. After stirring for 30 minutes, Emersol
- 25 210 oleic acid in an amount of 55.20 parts was added and the dispersion stirred for 30

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minutes more. Emersol 210 is available from Henkel Corp. Emery Division, Cincinnati, Ohio. The dispersion was further thinned with 1909.94 parts of deionized water, 1273.29 parts of deionized water and 2345.54 parts of deionized water in stages and vacuum stripped to remove organic solvent to give a dispersion having a solids content of 44.78 percent and a particle size of 860 Angstroms.

Example 1 Part C: Preparation of Cationic Electrocoat Primer

A cationic electrodeposition coating was prepared from the following materials. All parts and percentages are by weight unless otherwise indicated.

Material	Parts by Weight
Main Vehicle from Ex. 1B	1281.6
Co-Resin ⁵	120.3
Surfactant ⁶	2.5
Pigment Paste ⁷	589.2
Deionized Water	1806.4
Total	3800.0

⁵ An aqueous dispersion of a flexibilizer-flow control agent generally in accordance with U.S. Patent No. 4,423,166 was prepared for use with the electrodepositable composition. The flexibilizer-flow control agent was prepared from a polyepoxide (EPON828) and a polyoxyalkylene-polyamine (JEFFAMINE D-2000 available from Huntsman Corporation, Salt Lake City, Utah). The flexibilizer-flow control agent was dispersed in aqueous medium with the aid of lactic acid and the dispersion had a resin solids content of 36.0 percent.

⁶ A Surfactant blend (85-XS-139) available from Air Products and Chemicals, Inc., Allentown, Pennsylvania.

⁷ A cationic pigment paste (CP639) having an electroconductive carbon black pigment available from PPG Industries, Inc., Pittsburgh, Pennsylvania.

The cationic electrodepositable coating composition was prepared by adding the components in the order listed to a bath-type container for the coating of panels. The deposition of the composition involved immersing a zinc phosphated steel, a zinc phosphated electrogalvanized, and a zinc phosphated zinc-iron alloy panel in the bath and individually electrocoating the panels at 180 volts for two minutes at 95°F (35°C) in order to produce baked film builds of about 0.75 mil (19.0 microns). The electrocoated panels were baked 30 minutes at 365°F (185°C).

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Several chip resistant thermosetting polyurethane electrodepositable coating compositions were prepared as shown in the following Examples.

Example 2: Part A - Preparation of Anionic Polyurethane Resins

5 Anionic polyurethane resins were prepared from the materials listed in Table 1. All parts and percentages are by weight unless otherwise indicated.

Table 1

	All PolyTHF ⁸	Blend of polyTHF and Jeffamine	All polyPPO ⁹
	I	II	III
Polymeg 1000 ¹⁰	53.34	34.66	-
Niax 1025 ¹¹	-	-	34.77
polypropyleneglycol			
Isophoronediiisocyanate	31.77	33.54	33.41
Jeffamine D-2000	-	8.02	7.99
propoxylated	-	12.97	12.89
trimethylolpropane ¹² (pTMP)			
dimethylolpropionic acid	5.57	5.68	5.66
trimethylolpropane	6.05	-	-
Propylene glycol	3.27	3.05	3.21
1,4 butanediol	-	2.08	2.08
dibutyltindilaurate	0.02	0.02	0.02
methylisobutylketone (MIBK)	25	25	25
Total Resin Solids	100	100	100

⁸ polytetrahydrofuran

⁹ polypropylene oxide

10 ¹⁰ polytetrahydrofuran, 1,000 molecular weight, available from Great Lakes Chemical, Corp., West Lafayette, Indiana.

¹¹ polypropylene glycol, 1000 molecular weight, available from Arco Chemical Co. of Newton Square, Pennsylvania as PPG-1025.

15

¹² TS-30, available from Perstorp Polyols, Inc. Toledo, Ohio.

Preparation of Example 2I

Isophoronediiisocyanate (929.1 g, 8.37 equivalents "eq."), dibutyltindilaurate (0.58
20 grams "g."), and methylisobutyl ketone (145.6 g) were charged to a round bottom flask.

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The solution was heated to 50°C. At 50°C, Polymeg®1000 PolyTHF (1,535.4 g, 3.07 eq.) and MIBK (402.3 g) were added dropwise at a rate such that the temperature did not exceed 90°C. The reaction was held at 72°C for 45 minutes after the addition was complete and an isocyanate eq. wt. of 571 was obtained. At 72°C, dimethylolpropionic acid (162.8 g, 2.43 eq.) and MIBK (7.5 g) were added and the reaction was held at 90°C for an anticipated isocyanate equivalent weight of 1135. At the anticipated equivalent weight ("eq. Wt."), propylene glycol (95.8 g, 2.52 eq.), trimethylolpropane (177 g, 5.21 eq), and MIBK (168.9 g) were added and the reaction was held until no isocyanate remained (as determined by IR).

Generally, the polyurethane resins of II and III were prepared in a similar manner to that of I. Exceptions were that for II, Jeffamine D-2000 and pTMP were added rather than the PolyTHF alone. Likewise for example III the polypropylene glycol, Jeffamine D-2000, and pTMP were added and polyTHF was not added. Also for II and III, 1,4-butanediol was added in preparing the polyurethane resin.

Example 2: Part B Anionic Pigment Dispersing Resin

The following weight parts were combined:

	Material	Amount
1	Polymeg®2000 polyTHF ¹³	131.0
2	Fomrez®55-56 ¹⁴ polyester	131.0
3	1-methyl-2-pyrrolidinone	160.7
4	neopentyl glycol	10.2
5	dimethylolpropionic acid	54.1
6	Desmodur®W ¹⁵ polyisocyanate	235.1

¹³ poly(tetramethylene ether) glycol, Mw. = 2,000, available from Great Lakes Chemical Corp., West Lafayette, Indiana.

¹⁴ hydroxy terminated polyester, hydroxyl number 56, available from Witco Corporation, Endicott, New York.

¹⁵ methylene-bis-(4-cyclohexyl) diisocyanate, available from Bayer Corporation, Pittsburgh, Pennsylvania.

Materials 1-5 in the order and amounts indicated were charged to a reaction vessel. The mixture was then heated to 54°C. Desmodur®W polyisocyanate and 1-methyl-2-

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pyrrolidinone (19.0) were then added to the reactor at a rate such that the temperature did not exceed 85°C. After the addition of the polyisocyanate was complete, butanol (2.7) and dibutyltindilaurate (0.6) were added to the reactor. The solution was held at 85 to 90°C until a stalled isocyanate advancement was achieved (< 15 units/hr., theory isocyanate equivalent weight = 1,560). After the isocyanate (NCO) advancement stalled, the resin was dispersed into deionized water (992.9), dimethylethanol amine (35.0), and ethylene diamine (15.0) and the dispersion was held at 75°C for 30 minutes. After the 30-minute hold, the dispersion was cooled to 50°C. At 50°C, deionized water (38.8) and propylene imine (6.5) were added. The dispersion was then heated to 60°C and held at this temperature for four hours before cooling to room temperature.

Example 2 Part C: Anionic Polyurethane Pigment Paste

Part CI: Preparation of Neutralized Acid Catalyst:

Two neutralized acid catalyst formulations were made. For Example 2 Part CI(1) an amount of 284.93 grams dinonylnaphthalene sulfonic acid Nacure 1051, available as a fifty percent dinonylnaphthalene sulfonic acid in ethyleneglycolmonobutylether, from King Industries of Norwalk, Connecticut, were mixed with 30.32 grams of dimethylethanolamine. This gives a neutralized acid catalyst intermediate with a calculated solids of 45.19 weight percent. For Example 2 Part CI(2) 60.0 grams of dinonylnaphthalenesulfonic acid solution, Nacure 1051 and 6.68 grams of triethylamine were mixed together and diluted with 511.7 grams of deionized water to give a neutralized catalyst dispersion with a calculated solid of 5.19%.

Part CII: Preparation of Pigment Paste

The following two pigment paste formulations were prepared with the listed materials in amounts as weight parts. These materials were mixed with a Cowles blade and then dispersed with conventional pigment dispersing equipment to a Hegman reading of 7.5+:

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	CII(1)	CII(2)
Solvent free acrylic grind resin ¹⁶	-----	212.2
Acid intermediate of Example 2CI(1)	55.1	---
Anionic Pigment Dispersing Resin of Example 2B	766.4	---
triethylamine	-----	17.5
Carbon Black ^{17a (17b)}	27.9	15.5
Titanium Dioxide ^{18a (18b)}	634.7	634.7
Transparent Red Iron Oxide ¹⁹	74.6	84.9
Phthalo Blue ²⁰	9.4	10.6
Deionized water	200	480

¹⁶ Resin prepared with materials as described in Example A of U.S. Patent 5,530,043 to 100 percent solids.

^{17a} Raven 410 and ^{17b} Raven 1200 both available from Columbian Chemicals Company, Atlanta, Georgia.

^{18a} R-900 and ^{18b} R-960-38 both available from DuPont de Nemours Company, Delaware.

¹⁹ 1030-AC-1005 available from Cookson Matthey of Jacksonville, Florida.

²⁰ 248-0061 available from Sun Chemical, Inc., Linden, New Jersey.

For Example CII(1) after dispersion, the dispersing mill was rinsed with a small amount of deionized water. The resulting pigment paste had a measured solids (60 minutes at 110°C) of 57.3 percent.

Example 2 Part D: Preparation of Electrodepositable Thermosetting Anionic Polyurethane Formulations

The following formulations were made using polyurethane backbones from Example 2 Part A as indicated in Table 2, crosslinkers, and modifiers:

Table 2

	All Poly THF	Blend of polyTHF and Jeffamine	All poly PPO (polypropyleneoxide)	All polyTHF resin plus free PPO triol
Formulation	D1	D2	D3	D4
Resin from Example 2A	I	II	III	I
Amount of 2A Resin	268.8	268.8	268.8	237.5
Cymel 1135 ²¹	20	20	20	20
Cymel 1123 ²²	15	15	15	15
Polypropyleneoxide triol ²³	-	-	-	25
dimethylethanolamine	3.83	3.83	3.83	3.83
deionized water	550	550	550	550
Amount of flexibilizing segment	47.2	49.2	49.2	52.0
Ratio Polytetrahydrofuran to polypropylene oxide	∞	1.65/1	0	4.06

²¹ methoxy/n-butoxy melamine formaldehyde resins available from Cytec Industries Inc. West Patterson, New Jersey.

5 ²² methylated ethylated benzoguanamine resins available from Cytec Industries Inc.

²³ LHT-240, 720 molecular weight polypropyleneoxide triol available from Arco Chemical Co. of Newton Square, Pennsylvania.

Formulations D1-D4 were made using the following "hotmix" procedure:

10 The resin, crosslinkers, and amine were weighed into a quart sized stainless steel beaker, and the beaker placed in a water bath maintained at 80°C. The mixtures were stirred with an air motor and flat pitched propeller blade until homogeneous. Under continuous stirring, 550 grams of deionized water was added slowly to form an aqueous dispersion. After forming the aqueous dispersion, heat to the water bath was turned off, and the mixtures

15 were allowed to cool. The mixtures were transferred to open one gallon plastic containers and stirred overnight with magnetic stirring bars. After stirring overnight to allow most of the ketone solvent to evaporate, an additional 3490 grams of deionized water, along with 75.1 grams of pigment paste from Example 2Part CII(1) were added to complete the electrocoat bath formulations.

20 The calculation of the amount of flexibilizing segment in Table 2 of Example 2 Part D was determined in the following manner. The following are summed:

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polytetrahydrofuran, polyether diols, polyether diamines, polyether plasticizers, and any materials known to impart flexibility to coating films. For the total resins solids, all materials contributing to resin solids are summed, with the proviso that for the Cymel 1123 and Cymel 1135 amine-formaldehyde resins, a weight loss upon curing is estimated. A
5 weight loss for both Cymel 1123 and Cymel 1135 is estimated to be 20%, giving them estimated solids in a baked film of 80%.

As a sample calculation of flexibilizing segment content, the calculation for Formulation D1 is as follows:

	Solid resin materials from resin:	215 grams
10	Cymel 1135 (20 grams x .8)	16 grams
	Cymel 1123 (15 grams x .8)	12 grams
	Total	243 grams

Flexibilizing segments: 215 grams of resins solids x 53.34 % Polymeg 100 = 114.7 grams of Polymeg 1000. $114.7 / 243 = 47.2\%$ as the amount of flexibilizing segment. The other
15 amounts of flexibilizing segment for the other formulations were calculated in a like manner.

The determination of the weight loss upon curing of amine-formaldehyde resins can depend on many factors such as bake schedule, amount of acid catalysis, and amount of available co-reactants. Nevertheless, but can be estimated from a supplier's reported range
20 of equivalent weight. The equivalent weight of Cymel 1123 is reported to range from 130 to 190 grams per mole of reaction site. The molecular weight of Cymel 1123 benzoguanamine monomer is estimated as 391 by assuming equal moles of the alkylation alcohols, methanol and ethanol. Calculating a weight loss for two moles of methanol yields a calculated weight loss of 15.8 %. Calculating a weight loss for two moles of methanol
25 and one mole of ethanol yields a calculated weight loss of 27.4%. The calculations are only rough estimates of how an amine-formaldehyde resin will cure in a particular formulation. An estimate of 20% weight loss is applied to both Cymel 1123 and Cymel 1135 in the examples.

Examples 3 and 4

Two thermosetting anionic polyurethane electrodepositable compositions were prepared from the formulations shown in Table 3 where the amounts of the components are given in weight parts.

5

Table 3

Charge	Material	Example 3	Example 4
1	Isophoronediiisocyanate	922.4	461.6
2	Dibutyltindilaurate	0.55	0.28
3	MIBK	253.7	90.2
	Hold Temperature °C	70	50
4	Polymeg 1000	953.3	586.8
5	MIBK	238.3	146.7
6	1,4 butanediol	57.3	12.8
7	MIBK	---	11.3
8	Jeffamine D-2000	220.5	110.3
8A	MIBK	15	7.5
9	Dimethylolpropionic acid	156.3	78.9
10	MIBK	127.5	7.5
10A	propylene glycol	83.9	21.8
11	Propoxylated trimethylolpropane ¹² (pTMP)	356.9	
11	Trimethylolpropane	---	125.9
12	MIBK	71.1	75
13	MIBK	69.9	11.3
	Held		
	temperature of 93-95°C		
14	Dimethylethanolamine	52	
14A	Triethylamine	---	44.6
15	Paraplex WP-1 ²⁴		73.6
15A	Cymel 1123	191.9	---
16	Cymel 1135	256.2	---
16A	Cymel 1170		370.1
17	deionized water	2637.4	1536.6
18	deionized water	2475.14	1180.9

²⁴ propoxylated cresol plasticizer available from C.P. Hall company, Chicago, Illinois.

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Preparation of Anionic Polyurethane Formulation Stripped of Solvent

For Examples 3 and 4, the components listed in Table 3 were combined in a similar manner where any difference for Example 4 from Example 3 is indicated in parenthesis in the following description. The isophoronediiisocyanate, dibutyltindilaurate, and MIBK were charged to a reaction vessel. The mixture was heated to 70°C (50°C) under a nitrogen blanket with agitation. The POLYMEG® 1000, MIBK, 1,4-butanediol and JEFFAMINE® D2000 were added slowly, at a rate that kept the reaction temperature at or below 90°C. (For Example 4 the JEFFAMINE® D2000 was added slowly with a MIBK rinse to the three other materials after they were combined at a rate to keep the temperature below 90°C along with an MIBK rinse and held at 75°C for 27 minutes.) For Example 3 an MIBK rinse was also subsequent to the addition of JEFFAMINE® D2000 polyamine. The reaction was held at 75°C for 60 (27) minutes. An isocyanate equivalent weight (eq. wt.) of 556 (570) was obtained. Dimethylolpropionic acid followed by a rinse of MIBK was added, and the reaction mixture heated to 88°C. When the isocyanate eq. wt. reached 1185 (1132), propylene glycol, and propoxylated trimethylolpropane, for Example 3, or (trimethylolpropane), for Example 4, and MIBK were added to the reaction mixture and rinsed with MIBK. The reaction mixture was held at 100°C until the isocyanate was consumed (as determined by IR).

For Example 3, the reaction mixture was cooled to 93°C. For Example 4 the reaction was discontinued over night and heated the next day to 95°C. Dimethylethanolamine, and either CYMEL® 1123 and CYMEL® 1135 (or for Example 4 Paraplex WP-1 and CYMEL® 1170) were added and mixed for 10 minutes. For Example 3, the first addition of deionized water was made over one hour, and the dispersion was cooled to 60°C. This temperature was held for 30 minutes before the second addition of deionized water was made over 60 minutes while maintaining a temperature of 60°C. For Example 4 the first addition of deionized water was made to 93% of the above reaction over 34 minutes and the reaction was allowed to mix for 24 minutes. The second addition of deionized water was made over 47 minutes. Both dispersions were vacuum stripped at 60°C to remove solvent.

For Example 3 the composition was filtered using diatomaceous earth and adjusted with deionized water to a solids content of 34.1 (35.1 % weight percent for Example 4).

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For Example 3, an amount of 953.2 grams of this filtered resin was blended with 97.63 grams of the pigment paste of Example CII(1) and 2.75 liters of deionized water to complete the electrocoat bath formulation.

For Example 4 the anionic thermosetting polyurethane electrodepositable composition was prepared from the polyurethane of Example 4 and the catalyst dispersion of Example 2 Part CI(2) and the pigment paste of Example CII(2). This was performed under continuous agitation from a magnetic stirring bar in a plastic, one gallon sized container, where an amount of 880.7 grams of the polyurethane resin of Example 4 was diluted with 1.5 liters of deionized water. Also 24.66 grams of catalyst dispersion of Example 2 Part CI(2) were diluted with 100 grams of deionized water, and the beaker was rinsed with additional deionized water. An amount of 70.5 grams of the pigment paste of Example CII(2) were diluted with 50 grams, and the beaker rinsed with additional deionized water. Deionized water was added to increase the volume of the electrocoat bath to 3.5 liters, completing the formulation.

15

Testing of Electrocoat Compositions

Steel panels were coated with a conductive primer cationic electrocoat of Example 1, baked, and then electrocoated with bath formulations of Examples 2 and 3. The steel panels coated with a zinc-iron galvanizing layer, commonly referred to as electrozinc-iron, were pretreated by cleaning and phosphating with CHEMFOS C-700 phosphate pretreatment available from PPG Industries Inc., Pittsburgh, Pennsylvania. The resulting panels, supplied as part number APR-24526 by ACT Laboratories, Inc. of Hillsdale, Michigan, were coated with the conductive primer composition of Example 1. The panels were coated at 180 volts at 95.5°F (35.3°C) for 135 seconds, spray rinsed with deionized water, and baked for 30 minutes at 365°F (185°C) in a gas oven. A dry film thickness of 0.7 to 0.75 mils (17.8 to 19 microns) resulted.

After cooling, these primed panels were coated with the second, chip resistant electrocoats of Examples 2 and 3 at 160 volts at a temperature of 85°F (29°C). The coating time, bake temperature and film thickness varied between samples as shown in Table 4. During the second electrocoat operation, the panels were removed from the electrocoat bath and spray rinsed with deionized water in the usual manner of the electrocoating process. Furthermore, on the front side of the panel, a 0.1 % solution of Surfynol GA surfactant with

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an HLB of 13+ and a solution cloud point of 135°F, 57°C (available from Air Products and Chemicals Inc.) in deionized water was flowed over the freshly electrocoated film. After draining, the panels were baked by two methods: 30 minutes at 300°F (149 °C) in an electrically heated oven, and for 30 minutes at 320°F (160°C) in a gas fired oven.

- 5 Table 4 summarizes the results of testing for film defects and chip resistance. For testing chip resistance, panels were topcoated with NHU-90394/DCT-3000, a white acrylic-melamine topcoat of the basecoat/clearcoat type available from PPG Industries.

Table 4

Bath Formulation	2D1	2D2	2D3	2D4	3	2D1	2D2	2D3	2D4	3
Coating time, sec.	45	50	45	45	60	45	50	45	45	60
30 minute Bake	300°F Elec.	300°F Elec.	300°F Elec.	300°F Elec.	300°F Elec.	320°F Gas	320°F Gas	320°F Gas	320°F Gas	320°F Gas
Film thickness, mils (microns)	1.4 to 1.5 (35.6 to 38)	1.4 to 1.5 (35.6 to 38)	1.4 to 1.5 (35.6 to 38)	1.4 to 1.5 (35.6 to 38)	1.3 (33)	1.4 to 1.5 (35.6 to 38)	1.4 to 1.5 (35.6 to 38)	1.4 to 1.5 (35.6 to 38)	1.4 to 1.5 (35.6 to 38)	1.3 (33)
Craters per panel, front side ²⁵	90, 58, 63	3, 2, 5	1, 2, 1	6, 19, 14	5, 2, 0	13	1	2	4	1
Craters per panel, back side ²⁵	24, 29, 19	3, 4, 8	0, 4, 2	2, 5, 6	5, 0, 14	6	8	2	3	5
G.M. Gravelometer Chip ²⁶	9+	9+	9	9+	9	9+	9+	6	9+	9+
Kugelstoss ²⁷	1.6	1.0	14.4	1.9	9.4	1.0	1.4	10.7	1.5	7.9
3mm ball, 75 mph ²⁸	0.0	0.0	19.6	0.0	12.9	0.0	0.0	18.6	0.0	5.7
3mm ball, 95 mph ²⁸	2.7	1.9	21.6	2.2	14.4	1.4	2.1	19.3	1.7	15.7

²⁵ Multiple numbers represent replication, for example three separate panels. The film defects in these dried films were a common type of electrocoat defect, depressions in the shape of a crater which were counted.

²⁶ Chip Resistance using General Motors Engineering Standard GM9508P where the ratings given are on a scale of 0 to 9 with 0 being severely chipped and 9 representing outstanding chip resistance.

²⁷ For Kugelstoss testing, topcoated panels were stored in a freezer at -20°C for at least two hours, and then shot with a 2 mm chrome steel ball at a velocity of 155 miles per hour (249 km/hour). The ball impacted the coated test panel at 90°, or perpendicular to the surface. After removing from the freezer, raised and loosened portions of the paint system were removed with a sharp tool. The total area of damage was measured and the results reported in square millimeters of damage.

²⁸ For impact testing with 3 mm balls, the same method was used as with Kugelstoss, except that 3 mm chrome steel balls were shot at 75 miles per hour (121 km/hr.) and 95 miles per hour (153 km/hr.).

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The electrocoat bath of Example 4 was applied by electrocoating over a substrate which consisted of 0.74 mils (18.8 microns) of a cured, conductive black electrocoat on a phosphated electrozinc-iron steel panel. This electrocoat is available from PPG Industries Inc. Connecting the substrate as the anode, the composition of Example 4 was coated for 120 volts, at 85°F (29°C) bath temperature, for 50 seconds. After removal from the electrocoat bath, it was spray rinsed with deionized water in the usual manner. Furthermore, on the front side of the panel, a 0.1% solution of Surfynol GA surfactants in deionized water was flowed over the freshly electrocoated film. After draining, the panel was baked for 10 minutes at 200°F (93 °C) in an electric oven, the temperature of the oven set to 250°F (121°C), and the panel baked for an additional 20 minutes. A cured, solvent resistant coating resulted which had a film thickness of 1.29 mils (32.8 microns). After 100 double rubs with an acetone soaked cloth, only a trace dulling of the cured film was observed.

Comparative Examples 1 and 2

The following chip tests were done over a powder primer surfacer known in the industry to have excellent chip resistance, PCV-70100 available from PPG Industries, Inc. The substrate for the powder coating was Electrozinc-iron with a CHEMFOS 700/C20 phosphate pretreatment and a chrome rinse also available from PPG Industries Inc. After phosphating, the panels were coated with ED-5100 electrocoat (available from PPG Industries, Inc.), and then powder coated. The topcoat used for chip testing is the same as for Examples 2 and 3 above, NHU-90394/DCT-3000. Since the chip resistant coating was not electrodeposited there was neither a voltage nor a coating temperature and coating time of electrodeposition. After application of the topcoat on the chip resistant coating, the coatings were baked at 340°F (171°C) in an electric and gas-fired oven to give a film thickness of 3 mils (75 microns). Table 5 shows testing of this type of chip resistant coating in such a composite coating system of one coat electrocoated layer, spray applied chip resistant coating and topcoat layer.

Table 5

Formulation	Comparative Example 1 PCV-70100	Comparative Example 2 PCV-70100
Craters per panel, front side	2,5,1,2	3,8,9,6
Craters per panel, back side	Not Applicable	Not Applicable
G.M. Gravelometer Chip Rating	9+	9+
Kugelstoss	18.7	4.9
3mm ball @ 75 mph	9.7	1.4
3mm ball @ 95 mph	22.2	15.0
Cure	Electric	Gas

**Example 5: Preparation of Cationic Thermosetting Polyurethane
Electrodepositable Composition Cationic Pigment Paste for Cationic Polyurethane**

Example 5 Part A: Preparation of Cationic Polyurethane Resin

Isophoronediiisocyanate (1200.6 g, 10.82 eq.), methylisobutyl ketone (520.2 g), and dibutyltindilaurate (0.6 g) were charged to a round bottom flask. The mixture was heated to 30°C. Trimethylolpropane (125.1 g, 2.80 eq.) was then added to the solution. After the addition, the temperature rose to 73°C. Caprolactam (382.9 g, 3.38 eq.) and MIBK (40.0 g) were added to the flask. The mixture was maintained at 85°C until an isocyanate (NCO) eq. wt. of 490 was obtained. Terethane®650 is polytetrahydrofuran of 650 molecular weight which is available from DuPont. An amount of this PolyTHF of (707.9 g, 2.21 eq.) and MIBK (275.7 g) were then added to the flask. The addition was made at a rate such that the temperature was maintained below 90°C. After the addition was complete, the temperature was allowed to drift down to 65°C. At 65°C, Jeffamine®D2000 (437.0 g, 0.44 eq.), and MIBK (40.0 g) were added and the mixture was held for 15 minutes. After the hold, an NCO eq. wt. of 1974 was obtained. Diethanolamine (87.0 g, 0.83 eq.) and 125g aminopropyldiethanolamine (125.2 g, 0.77 eq.) were then added to the reaction mixture. The solution was held at 80°C until no NCO was present by IR analysis. After the isocyanate was consumed, 31g Surfynol®

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GA surfactant (30.7 g) and MIBK (40.0 g) were added and the solution was mixed for 15 minutes. The resin was then dispersed into deionized water (1,666.0 g) and dimethylolpropionic acid (82.9 g, 0.62 eq). The resin was further thinned with deionized water (3,303.0 g), resulting in a final dispersion at 36.5% solids. The dispersion was subsequently
5 vacuum stripped at 60°C to remove solvent.

Example 5 Part B

The following materials were mixed with a Cowles blade and then dispersed with conventional pigment dispersing equipment to a Hegman reading of 7+:

Epoxy grind resin ²⁹	1466.1
Deionized water	294.7
Titanium Dioxide ³⁰	1166.4
Transparent Red Iron Oxide ³¹	137.2
Phthalo Blue ³²	17.2
Carbon Black ³³	51.5

10 ²⁹ Sulfonium-quaternary ammonium type described in U.S. Patent No. 5,130,004 (PPG Industries, Inc., Johnson & McCollum) with a solids content of 31.2 percent.

³⁰ See footnote 18a.

³¹ See footnote 19.

15 ³² See footnote 20.

³³ See footnote 17a.

The resulting pigment paste had a calculated solid content of 58.4 weight percent.

Example 5 Part C: Cationic Polyurethane Electrocoat Composition

20 1067.9 grams of the resin of example 5 Part A was blended with 105.8 grams of the pigment paste of example 5 Part B and diluted with water to a total volume of 3.8 liters.

Testing of Cationic Polyurethane Electrocoat

The same type of steel panel from Examples 2 and 3, phosphated electrozinc-iron, was
25 electrocoated with the conductive primer of Example 1 and baked for 30 minutes at 365°F

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(185°C) in a gas oven to give a dry film thickness of 0.7 to 0.75 mils (17.8 to 19 microns). A dry film thickness of 0.7 to 0.75 mils (17.8 to 19 microns) resulted. The coating conditions here were for coating add in and may not have been similar to those of aforementioned examples.

- 5 After cooling, this primed panel was electrocoated with the cationic polyurethane electrocoat bath of Example 5. After the second electrocoat operation, the panel was removed from the electrocoat bath and spray rinsed with deionized water in the usual manner of the electrocoating process. Furthermore, on the front side of the panel, a 0.1 % solution of Surfynol GA surfactants in deionized water was flowed over the freshly electrocoated film.
- 10 After draining, the panel was baked for 30 minutes at 350°F (177°C) in an electric oven. It was topcoated with the same topcoat system used in Example 3, NHU-90304/DCT-3000 available from PPG Industries Inc. Test results are summarized in Table 6.

Table 6

Formulation	Cationic Polyurethane of Example 5
Coating voltage	175
Coating Temperature, °F (°C)	86 (30)
Coating time, sec.	95
Film thickness, mils (microns)	1.2 (30.5)
Craters per panel, front side	Not Available
Craters per panel, back side	2
G.M. Gravelometer Chip Rating	9+
Kugelstoss	1
3mm ball @ 75 mph	0
3mm ball @ 95 mph	1

15

Comparing the results of the electrodeposited thermoset anionic polyurethane chip resistant coating of Table 4 and the electrodeposited thermoset cationic polyurethane of Table 6 with the commercial spray chip resistant coating of Table 5 indicates that the

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electrodeposited coating compositions of the present invention and the resultant composite coatings can perform better than the commercially available spray coatings. Particularly from the results in Table 4 it can be seen that the polyurethane coatings of this invention can result in excellent chip resistance. The resistance to high speed impacts, are superior for the
5 polyurethane chip resistant electrodeposited coatings of the present invention versus that of a commercial primer surfacer, which is an important improvement.

The Gravelometer Chip results between the electrodeposited coatings and the spray indicated equal excellent performance except for a slightly inferior but acceptable performance of the anionic polyurethane without polytetrahydrofuran and with polypropylene oxide polymer
10 flexibilizing segment. For the Kugelstoss and impact tests all of the electrodeposited coatings with polytetrahydrofuran flexibilizing segments performed better than the commercially available sprayed chip resistant coating. The use of polytetrahydrofuran is particularly useful. When polytetrahydrofuran is omitted, as in example 2D3 of Table 4, chip resistance, although still worthwhile, decreases, as evidenced by larger areas of damage from ball impacts.
15 Particularly, it is desirable for the Kugelstoss test to have less than 8 square millimeters of damage. Also the electrodeposited coating with all polypropyleneoxide flexibilizing segments performed comparably to that of the commercially available spray chip resistant composition. The data also show that including some polypropylene oxide in the formulation, either built into the polymer as in example 2D2 Table 2, or added as free polyol as in Example 2D4 Table
20 4, is beneficial for film appearance and a reduction in crater defects. Thus, a combination of polytetrahydrofuran and polypropylene oxide in the formulations of this invention provide both good chip resistance and film appearance.

The composition of the present invention may also be applied to a substrate as a sprayable coating, as set forth in Example 6.

25

Example 6: Sprayable Cationic Polyurethane

Example 6 Part A: Preparation of Cationic Polyurethane Resin

Isophoronediiisocyanate (1215.6 g, 10.95 eq.), methylisobutyl ketone (433.4 g), and trimethylolpropane (135.7 g, 3.04 eq.) were charged to a round bottom flask. The mixture was
30 heated to 30°C. Dibutyltin dilaurate (0.63 g) and methylisobutyl ketone (15.0 g) was then

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added to the solution. After the addition, the temperature rose to 77°C. The temperature of the mixture was maintained at 85°C until an isocyanate (NCO) eq. wt. of 230.5 was obtained. Terethane®650 (725.8 g, 2.25 eq.), available from DuPont, and methylisobutyl ketone (106.0 g) were then added to the flask. The temperature of the mixture was maintained at 77°C until the NCO eq. wt. of 464.4 was obtained. Caprolactam (364.8 g, 3.22 eq.) was added to the flask and the reaction temperature increased to 85°C. The temperature of the mixture was maintained at 85°C until an isocyanate (NCO) eq. wt. of 1210 was obtained. The temperature of the reaction was cooled to 65°C. At 65°C, Jeffamine®D2000 (441.6 g, 0.44 eq.) was added and the mixture was stirred for 15 minutes. After this time, diethanolamine (88.1 g, 0.87 eq.), aminopropyldiethanolamine (126.8 g, 0.78 eq.) and methylisobutyl ketone (100.4 g) were added to the reaction mixture. The temperature of the solution was maintained at 80°C until no NCO was present by IR analysis. After the isocyanate was consumed, Surfynol® GA surfactant (31.0 g) and MIBK (8.1 g) were added and the solution was mixed for 15 minutes. The resin was then dispersed into deionized water (1946.4 g) and dimethylolpropionic acid (83.0 g, 0.62 eq.). The resin was further thinned with deionized water (3300.0 g), resulting in a final dispersion at 35.1% solids. The dispersion was subsequently vacuum stripped at 60°C to remove solvent to afford a dispersion at 47.2% solids.

Example 6 Part B: Preparation of Pigment Paste

The following materials were mixed with a Cowles blade and then dispersed with conventional pigment dispersing equipment to a Hegman reading of 7+:

Epoxy grind resin ³⁴	1466.1
deionized water	294.7
Titanium Dioxide ³⁵	1166.4
Transparent Red Iron Oxide ³⁶	137.2
Phthalo Blue ³⁷	17.2
Carbon Black ³⁸	51.5

³⁴ Sulfonium-quaternary ammonium type described in U.S. Patent No. 5,130,004 (PPG Industries, Inc., Johnson & McCollum) with a solids content of 31.2 percent.

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³⁵ R-900 available from DuPont de Nemours Company, Delaware.

³⁶ 1030-AC-1005 available from Cookson Matthey of Jacksonville, Florida.

³⁷ 248-0061 available from Sun Chemical, Inc., Linden, New Jersey.

³⁸ Raven 410 available from Columbian Chemicals Company, Atlanta, Georgia.

5

The resulting pigment paste had a calculated solid content of 58.4 weight percent.

Example 6 Part C: Sprayable Cationic Polyurethane Composition

143.5 grams of the resin of Example #6 Part A was blended with 13.5 grams of
10 pigment paste of Example #6 Part B and diluted to 26" on a #4 Ford with 5 grams of water.

Testing of Sprayable Cationic Polyurethane Composition

The composition listed in Part C was then hand spray applied to a 4"x12" ACT panel
already coated with electrocoat primer (ED5000, commercially available for PPG Industries,
15 Inc.). The sample was then cured at a temperature of 350°F for 30 minutes. The dry film
thickness of the primer was 1.22 mils.

The panel coated with the composition in Part C was tested for hardness using a Konig
Hardness Tester, and Gloss, Distinctness of Image, and Orange Peel using an QMS-BP, supplied
by Autospect Quality Measurement Systems. The sample had the following readings:

20 60° Gloss – 67 units
 DOI – 74.9
 Orange Peel – 55.7
 Hardness – 88 seconds

25 The sample coated with Part C was topcoated with Magmared Solventborne Monocoat
(Commercially available from PPG Industries Lacke GmbH) and baked at 285°F for 30 minutes
for a DFT of 1.74 mils. The Magmared topcoat was then applied to itself as a second coat (repair
coat) and baked at 285°F for 30 minutes for an additional DFT of 1.74 mils.

This total system was then chipped (multichip) using the Erichson chip method
30 (STM-0802, 2 x 2000 grams of shot at 30 psi). The resulting panel was rated <1 on a scale of
0-10 with 0 being the best.

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It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications that are within the spirit and scope of the invention, as
5 defined by the appended claims.

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WE CLAIM:

1. A process of coating a substrate, comprising:

- 5 (a) applying a first coating composition comprising at least one curable resin to at least a portion of a surface of a substrate to form a first coating thereon;
- (b) at least partially curing the first coating;
- 10 (c) applying a second coating over at least a portion of the first coating, the second coating being deposited from a composition comprising a curable polyurethane resin that contains a polymeric segment derived from an active hydrogen-containing polymer having a glass transition temperature of 0°C or less and a number average molecular weight of 400-4000 grams per mole; and
- 15 (d) at least partially curing the second coating.

2. The process of claim 1 wherein the second coating composition is substantially solvent free.

20 3. The process of claim 1 in which the polyurethane resin is prepared from components comprising:

- (a) a polyisocyanate, and
- (b) an active hydrogen-containing polyether.

25 4. The process of claim 3 wherein the components from which the polyurethane resin is prepared further comprise component (c) which is an active hydrogen-containing compound that contains a group that can be converted to an ionic group.

5. The process of claim 4 in which component (c) is an active hydrogen-containing compound that contains carboxylic acid groups or amino groups.

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6. The process of claim 4 wherein the components from which the polyurethane resin is prepared further comprise component (d) which is an active hydrogen-containing compound having a molecular weight below 400.

5

7. The process of claim 3 in which the polyisocyanate is an aliphatic or cycloaliphatic polyisocyanate.

8. The process of claim 3 in which the active hydrogens of the active hydrogen-
10 containing polyether are hydroxyl or primary amine.

9. The process of claim 3 in which the active hydrogen-containing polyether comprises (i) a polyoxytetramethylene diol.

10. The process of claim 9 in which the active hydrogen-containing polyether
15 further comprises (ii) a polyoxypropylene polyol or polyoxypropylenepolyamine.

11. The process of claim 10 in which the weight ratio of (i) to (ii) is 0.5-10:1.

12. The process of claim 3 in which (b) is present in an amount of at least thirty
20 (30) percent by weight of the components from which the polyurethane resin is prepared.

13. The process of claim 7 in which the polyisocyanate is selected from the group
consisting of isophorone diisocyanate, 1,6-hexamethylene diisocyanate, and isocyanurates
25 thereof.

14. The process of claim 1 in which the curable polyurethane contains active
hydrogens and the second coating composition comprises a curing agent having groups that are
reactive with the active hydrogens.

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15. The process of claim 14 in which the curing agent is an aminoplast or a capped polyisocyanate.

5 16. The process of claim 1 wherein the second coating composition further comprises an opacifying pigment.

17. The process of claim 16 wherein the opacifying pigment is selected from the group consisting of non-transparent iron oxides and transparent iron oxides.

10

18. The process of claim 1 wherein the second coating composition contains a hindered amine light stabilizer.

19. The process of claim 9 in which the active hydrogen-containing polyether
15 further comprises an oxyalkylated triol.

20. The process of claim 1 in which the polyurethane resin further contains a segment derived from a polymeric polyol selected from polyester polyols and polycarbonate polyols.

20

21. The process of claim 1 in which the first coating composition is applied to at least a portion of the surface of the substrate by cationic electrodeposition.

22. The process of claim 21 in which the second coating composition is spray
25 applied over at least a portion of the first coating.

23. The process of claim 1 in which the second coating composition is applied to at least a portion of the surface of the substrate by anionic electrodeposition.

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24. The process of claim 23 in which the second coating composition is an anionic composition that further comprises an aminoplast curing agent.

25. The process of claim 24 in which the aminoplast curing agent is present in the
5 second coating composition in an amount of from 5 to 50 percent by weight based on weight of resin solids.

26. The process of claim 1 in which the second coating composition is deposited
from a cationic electrodepositable coating composition.

10

27. The process of claim 26 in which the second coating composition is derived
from an active hydrogen-containing cationic electrodepositable composition that further contains
a capped polyisocyanate curing agent.

15 28. The process of claim 27 in which the polyisocyanate is capped with caprolactam
and/or dibutylamine.

29. The process of claim 27 which has an NCO/active hydrogen equivalent ratio of
1.0 to 1.5:1.

20

30. The process of claim 1 wherein the first coating composition has resistivity of
less than 10^{12} ohms-centimeters.

31. The process of claim 1 wherein the first coating composition is at least partially
25 cured by infrared radiant heating.

32. The process of claim 31 wherein the infrared radiant heating is directed to a
predetermined area of the first coating composition.

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33. The process of claim 32 wherein the substrate is a body for a motor vehicle with internal and external metallic surfaces and the first coating composition is partially cured by directing infrared radiant heating to the external metallic surfaces coated with the first coating so as to partially cure the coating on the exterior metallic surface, while leaving the first
5 coating on the interior surface essentially uncured.

34. The process of claim 33 wherein the infrared heating is for a time of between 10 seconds and 2 hours.

10 35. The process of claim 34 wherein prior to infrared heating the first coating composition is subjected to convection heating under conditions sufficient to remove water but insufficient to produce a conductive coating.

15 36. The process of claim 1 wherein the partial curing is at a temperature in the range of 120°C to 220°C (248°F-428°F).

20 37. The process of claim 1 wherein the conductive substrate is selected from the group consisting of steel, zinc, aluminum, copper, magnesium, galvanized metals, hot dip galvanized steel and electrogalvanized steel.

38. The process of claim 1 wherein the first coating composition is spray applied onto the substrate.

25 39. The process of claim 38 wherein the second coating composition is spray applied onto at least a portion of the first coating.

40. An electrically conductive article coated by the process of claim 1.

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41. A substantially solvent free aqueous composition comprising a curable polyurethane resin containing ionic salt groups dispersed in an aqueous medium, the polyurethane resin being prepared from the components comprising:

- (a) a polyisocyanate, and
- 5 (b) an active hydrogen-containing polymer having a glass transition temperature of 0°C or less and a number average molecular weight of 400-4000.

42. The aqueous dispersion of claim 41 in which the polyisocyanate is an aliphatic
10 or cycloaliphatic polyisocyanate.

43. The aqueous dispersion of claim 41 in which (b) is an active hydrogen-containing polyether.

15 44. The aqueous dispersion of claim 41 in which (b) comprises a mixture of (i) polyoxytetramethylene diol and (ii) polyoxypropylene polyol in which the weight ratio of (i) to (ii) is from 0.5-10:1.

45. The aqueous dispersion of claim 41 in which (b) is present in an amount of at
20 least 30 percent by weight based on weight of reactants used to make the polyurethane.

46. The aqueous dispersion of claim 41 wherein the components from which the polyurethane resin is prepared further comprise component (c) which is an active hydrogen-containing compound having a molecular weight below 400.

25

47. The aqueous dispersion of claim 41 in which the curable polyurethane resin has active hydrogen groups and a curing agent having groups that are reactive with the active hydrogens.

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48. The aqueous dispersion of claim 41 in which the curing agent is an aminoplast or a capped polyisocyanate.

49. The aqueous dispersion of claim 48 in which the capped polyisocyanate is
5 capped with caprolactam and/or dibutylamine.

50. The aqueous dispersion of claim 48 in which the capped polyisocyanate is integral with the polyurethane backbone.

10 51. The aqueous dispersion of claim 41 in which the components used to prepare the polyurethane comprise an active hydrogen and a group which can be converted to an ionic salt group.

52. The aqueous dispersion of claim 51 in which the group is carboxylic acid or
15 amine.

53. The aqueous dispersion of claim 41 in which the curable polyurethane comprises carboxylate salt groups and an aminoplast curing agent.

20 54. The aqueous dispersion of claim 41 further comprising an opacifying pigment.

55. The aqueous dispersion of claim 41 further comprising a hindered amine light stabilizer.

25 56. The aqueous dispersion of claim 41 wherein the dispersion may be applied to a substrate by a coating process selected from the group consisting of spray coating and electrophoretic coating.

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57. The aqueous dispersion of claim 41 having a resin solids content of 5 to 50 percent by weight.

58. A substantially solvent free cationic aqueous composition comprising an active hydrogen-containing polyurethane resin having cationic salt groups dispersed in an aqueous medium; the polyurethane being the reaction product of:

- (a) an aliphatic or cycloaliphatic polyisocyanate,
- (b) an active hydrogen-containing polyether which comprises a mixture of:
 - (i) a polyoxytetramethylene diol and
 - (ii) a polyoxypropylenepolyamine;the weight ratio of (i) to(ii) being from 0.5 to 10:1,
- (c) an active hydrogen group containing a tertiary amine group;

the polyurethane being at least partially neutralized with acid; the dispersion also containing a capped polyisocyanate curing agent.

59. The aqueous dispersion of claim 58 in which the capped polyisocyanate is capped with caprolactam and/or dibutylamine.

60. The aqueous dispersion of claim 58 in which the capped polyisocyanate is integral with the polyurethane backbone.

61. The aqueous dispersion of claim 58 which has an active hydrogen/isocyanate equivalent ratio of 1 to 1.5:1.

62. The aqueous dispersion of claim 58 wherein the dispersion may be applied to a substrate by a coating process selected from the group consisting of spray coating and electrostatic coating.

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63. A process of coating a substrate, comprising:

- (a) electrodepositing an electrically conductive first coating composition comprising a curable ionic resin and an electroconductive pigment;
- (b) at least partially curing the electrodeposited coating composition so as to make the coating electrically conductive;
- (c) applying a second coating composition on at least a portion of the electrodeposited coating, the second coating composition being a curable polyurethane resin that contains a polymeric segment derived from an active hydrogen-containing polymer having a glass transition temperature of 0°C or less and a number average molecular weight of 400-4000 grams per mole; and
- (d) at least partially curing the second coating.

64. The process of claim 63, wherein the second coating composition is

substantially solvent free.

65. A multicomponent composite coating, comprising:

- (a) a first coating composition applied on at least a portion of a substrate, the first coating composition comprising a curable resin; and
- (b) a second coating composition applied over at least a portion of the first coating composition, the second coating composition comprising a curable polyurethane resin that contains a polymeric segment derived from an active hydrogen-containing polymer having a glass transition temperature of 0°C or less and a number average molecular weight of 400-4000 grams per mole.

66. The multicomponent composite of claim 65, wherein the second coating composition is substantially solvent free.

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67. The multicomponent composite of claim 66, wherein the second coating composition is spray applied over the first coating composition.

68. A coated substrate comprising the multicomponent composite coating of
5 claim 65.

69. A multicomponent composite coating, comprising:

(a) an electrically conductive first coating composition applied on at least a portion of a substrate, the first coating composition comprising a
10 curable ionic resin and an electroconductive pigment; and

(b) a second coating composition applied over at least a portion of the electrodeposited coating composition, the second coating composition comprising a curable polyurethane resin that contains a polymeric
15 segment derived from an active hydrogen-containing polymer having a glass transition temperature of 0°C or less and a number average molecular weight of 400-4000 grams per mole.

70. The multicomponent composite of claim 69, wherein the second coating composition is substantially solvent free.

71. The multicomponent composite of claim 70, wherein the second coating composition is spray applied over the first coating composition.

72. A coated substrate comprising the multicomponent composite coating of
25 claim 69.

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(57) Abstract: A process for applying two coatings, one on top of the other, to a substrate is provided. A first coating is applied to
provide corrosion resistance and a second polyurethane-based coating is applied to the first coating to provide chip resistance. Also,
aqueous dispersions of the polyurethane coating compositions are disclosed.

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A. CLASSIFICATION OF SUBJECT MATTER

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 905 132 A (GROSS LUTZ-WERNER ET AL) 18 May 1999 (1999-05-18) column 1, line 59 -column 2, line 67 column 8 -column 11; claims 1,5; table 1	1,2, 14-16, 22,24, 25,37, 40-42, 45,47, 48, 51-53, 56,57, 65-67
X	US 6 077 960 A (CHEN KAN-NAN ET AL) 20 June 2000 (2000-06-20)	41-43, 45-48, 50-52,56
A	column 1, line 61 -column 6, line 44; examples 1,2	44,53

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